Nanotechnology Based Environmentally Robust Primers

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NANOTECHNOLOGY
BASED ENVIRONMENTALLY ROBUST PRIMERS

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Abstract

An initiator device structure consisting of an energetic metallic nano-laminate foil coated with a sol-gel derived energetic nano-composite has been demonstrated. The device structure consists of a precision sputter deposition synthesized[1] nano-laminate energetic foil of non-toxic and non-hazardous metals along with a ceramic-based energetic sol-gel produced coating made up of non-toxic and non-hazardous components such as ferric oxide and aluminum metal.**[2]** Both the nano-laminate and sol-gel technologies are versatile commercially viable processes that allow the "engineering" of properties such as mechanical sensitivity and energy output. The nano-laminate serves as the mechanically sensitive precision igniter and the energetic sol-gel functions as a low-cost, non-toxic, non-hazardous booster in the ignition train. In contrast to other energetic nanotechnologies these materials can now be safely manufactured at application required levels, are structurally robust, have reproducible and engineerable properties, and have excellent aging characteristics.

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Introduction

Many energetic systems can be activated via mechanical means. Percussion primers in small caliber ammunition and stab detonators used in medium caliber ammunition are two examples of this. A mix of energetic powderssensitive to mechanical stimulusis typically used to ignite any such device. Rapid heating caused by mechanically driven compression and friction of the mixture results in its ignition. The rapid decomposition of these materials generates a pressure/temperature pulse that is sufficient to initiate a transfer charge, which has enough output energy to detonate the main charge. Thisignition mix is used in a large variety of primers, igniters, and detonators.**[3]**

Common primer mixes, such as NOL-130, are made up of lead styphnate (basic) 40%, lead azide (dextrinated) 20%, barium nitrate 20%, antimony sulfide 15%, and tetrazene 5%.**[3]** These materials pose acute and chronic toxicity hazards during mixing of the composition and later in the item life cycle after the item has been field functioned. There is an demonstrated need to replace these mixes on these toxicity grounds.

We have demonstrated and are further developing mechanically initiated initiator devices that consist of macroscopic energetic nano-laminate metallic foils coated with a sol-gel derived energetic nano-composites. These initiator devices can be used as precision non-toxic alternatives to current initiator technologies. The devices are made up of a precision energetic foil of non-toxic and non-hazardous metal nano-laminates single side coated with an energetic sol-gel coating made up of non-toxic and non-hazardous components such as ferric oxide and aluminum metal. Both the nano-laminate and sol-gel technologies are based on versatile commercially viable processes that enable the "engineering" of salient properties including sensitivity and energy output.**[3-5]**

The nano-material sol-gel and sputtering approaches to energetic materials fabrication offer precision control of composition and morphology, variables important for both safety and for reaction rates. This characteristic of these nano-material synthesis capabilities has not been achieved with either conventional materials or other nano-materials based approaches. Such control enables the creation of generically new energetic initiator materials with desirable properties.

At LLNL nano-laminates have been synthesized by magnetron sputter deposition physical vapor deposition from at least 75 of the 92 naturally occurring elements in elemental form, as alloys or as compounds. Although nano-laminate materials are not typically described by the terms nano-structure or nano-phase they are clearly high interface concentration ultra-fine grained low contamination solids. Nano-structure or nano-phase materials are ultra-fine grained high interface concentration materials. They are characterized by truly nano-scopic structures and thus, large interfacial area to volume ratios. Understanding of the effects of this high interface concentration on properties is primary to the understanding of these materials. The research, development and applications program at Lawrence Livermore National Laboratory has sought to bring this new class of matter into high payoff applications use and then to broaden the application of the technologies developed to new areas. We have, in a very general sense, focused a significant part of our effort on the interfaces in these new materials as that is their unique characteristic and in many cases is a determining factor in scientific investigations and technological performance. This interface focus resulted in the engineering development of energetic nano-laminate foils at LLNL and the development of both a phenomenological and a fundamental understanding of the important materials and nano-structural features resulting in the observed energetic behavior.

Magnetron sputtering was used to prepare the nanolaminates applied here. In sputter deposition systems atoms, or clusters of atoms, are generated in the vapor phase by bombardment of a solid source material with energetic inert gas ions. The sample substrate is moved past the source(s), metal vapor condensing on the substrate to form a film. Layers of each material are sequentially deposited on the substrate with each pass past the individual magnetron sputter sources. The thickness of each component layer is precisely controlled by adjusting the periodicity of substrate movement as well as the excitation of the sputter sources. At the limit where the individual layers are less than 0.5 atomic monolayer thick compositionally homgeneous foils are fabricated. When the layers are substantially thicker than one monolayer and composed of materials which exothermally react to form intermetallic compounds energetic nano-laminates are fabricated.

TABLE 1: Thermodynamics of Selected Intermetallic Compound Formation Reactions

Reaction	Heat of Reaction (kJ per mole atoms)	Calculated Adiabatic Reaction Temp. (°C)	Reaction Product Phases
Zr + Al -> ZrAl	-45	1480	solid & liquid
Ti + Al -> TiAl	-36	1227	solid
Ni + Al -> NiAl	-59	1639	solid & liquid

Several nano-laminate aluminum/transition metal candidates have been investigated. Thermodynamic properties and calculated adiabatic reaction temperatures for aluminum/zirconium, aluminum/titanium and aluminum/nickel are presented in Table 1. The adiabatic temperatures are seen to be high. We note here that measurements of the adiabatic reaction temperature for an Al-25.4 at% Zr yielded a value of 1400°C ± 50. This is in reasonable agreement with the predicted value of 1480°C as expected from the Differential Scanning

Calorimeter data presented in Table 2. The total exothermic heat for the Al-25.4 at% Zr sample was 46.5 ± 3.5 kJ/mole atoms, being essentially equal to the value of 45 kJ/mole atoms used in the adiabatic temperature calculation. Though the Al/Zr system is very promising the initiator work described here was done using Al/Monel400 nano-laminates fabricated over seven years ago and simply stored in a filing cabinet since then. Experimental results for this material system, Monel440/Al, will be presented in the results section of this paper.

Table 2: Phases formed and total exothermic heat determined by Differential Scanning Calorimetry for Al/Zr nano-laminates as a function of increasing Zr concentration

Composition	Products of Reactions		ΔH_f
(at% Zr)	(Expected)	(Obtained)	(kJ/mol atoms)
7.6	Al & Al_3Zr	Al & Al_3Zr	16.6 ± 0.7
25.4	Al_3Zr & Al_2Zr	Al_3Zr & Al_2Zr	46.5 ± 3.5
30.5	Al_3Zr & Al_2Zr	Al_3Zr & Al_2Zr	51.4 ± 3.6
46.8	$AlZr$ & Al_3Zr_2	Al_3Zr_2	52.1 ± 0.9*
63.7	$AlZr_2$ & Al_3Zr_2	$AlZr_2$	36.2 ± 3.2

Shelf life or environmental sensitivitiy are major issues that may prove to be an insurmountable obstacle to other approaches to the development of nanostructure based initiators; ie. initiators using nanometer metal fuel powders (i.e., MIC materials) in the initiating mix.[8-10] Nanometric fuel metal particles are extremely sensitive to hydrolysis and can oxidize rapidly under humid and warm conditions if the particles have not been specially coated Additionally, production of these highly reactive materials at bulk levels has not been demonstrated.

The sol-gel techniques developed at LLNL, provide a different approach to the preparation of energetic materials. LLNL was the first to appreciate that this methodology enables a the control of the morphology, size, and composition of components of energetic nanocomposites as well as enhancing their intimate mixing.[11-15] We have reported on the application of sol-gel techniques to energetic materials synthesis and processing. Using the sol-gel methodology structural and compositional parameters can be manipulated on the nanoscale. This has enabled the establishment of new energetic materials with new and potentially useful properties. With this method come new potential benefits of added safety, reproducibility, versatility, and low hazardous waste generation.

Experimental Approach

Sol-gel energetic compositions were dip coated onto the Monel400/Al nano-laminate substrates. The nano-laminate thickness was $\approx$ 25 μm in all the experiments reported here. A sheet of Monel400/Al nano-laminate was cut with scissors to form strips that were 0.5 cm x 10 cm.   The Monel400/Al nano-laminate used was prepared seven years ago and has been stored under ambient conditions since then.

A sol of Fe_2O_3 nanoparticles was prepared using methods reported previously.[12-15] Sol aluminum powder was added to the Fe_2O_3 nanoparticle sol while stirring the entire mixture to ensure good mixing of components. Once the mixture had suitably thickened 2 to 3 cm lengths of the nano-laminate stripls were dipped into the mixture and withdrawn quickly. The deposited sol-mixture rapidly dried to give a uniform coating of thermite (Fe_2O_3/Al) on the nano-laminate foil. The coated nanolaminate strips were allowed to dry overnight in a fume hood.

Once dry the coated nanolmainates were reliably ignited via mechanical stimulus. A spring-loaded punch was used to stimulate the uncoated end of the

nanolaminate. The nanolaminate was observed to react and the reaction propagated down the length of the strip to the end where the more energetic thermite coating was ignited. The thermite burn resulted in the ejection of hot particles.
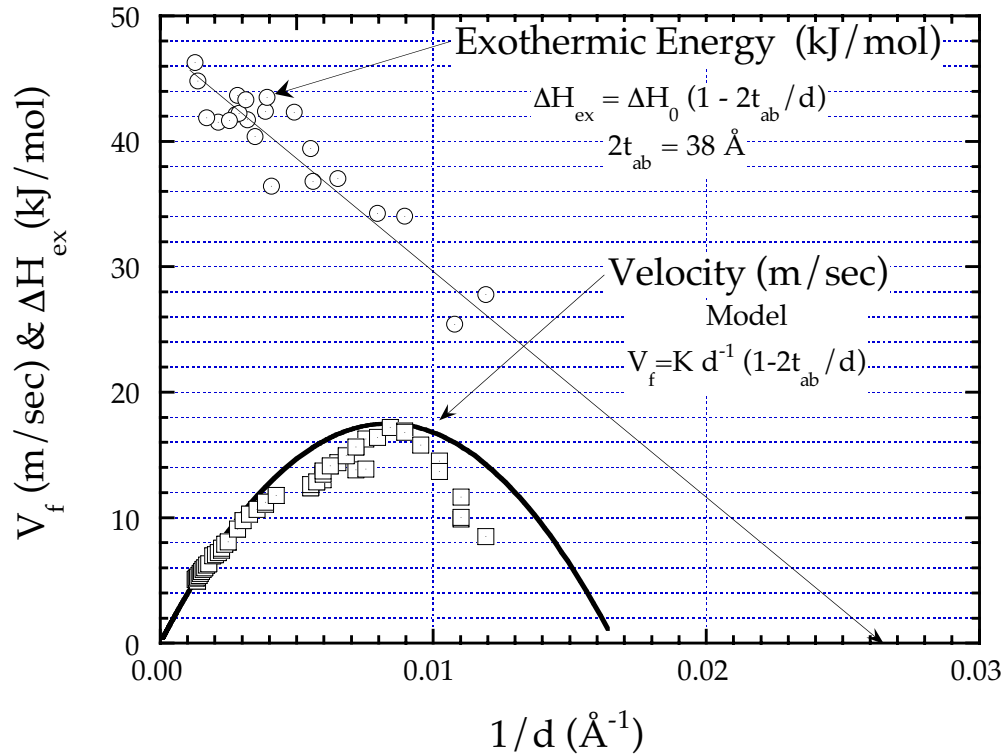

The figure is a plot with x-axis "$1/d$ (Å^{-1})" ranging from 0.00 to 0.03, and y-axis "V_f (m/sec) & ΔH_{ex} (kJ/mol)" ranging from 0 to 50. It shows:

Exothermic Energy (kJ/mol)
$$\Delta H_{ex} = \Delta H_0 (1 - 2t_{ab}/d)$$
$$2t_{ab} = 38 \text{ Å}$$

Velocity (m/sec)
Model
$$V_f = K\, d^{-1} (1 - 2t_{ab}/d)$$

Figure 1: The nano-laminate period (d) dependencies of the experimentally determined Reaction Front Velocity (V_f - m/sec) and the Total Exothermic Energy (ΔH_{ex} - J/mole atoms) are presented and compared to model calculations for Monel400/Al {$(Ni_{0.7}Cu_{0.3})Al$} nano-laminate structures.

Results

Nano-laminate metal materials can be prepared with engineered to have

specific reaction front velocities, energy release rates, ignition temperatures and total stored exothermic energy. For example, the reaction front velocity of a nano-laminate depends on the nano-laminate period as shown in Figure 1. In this figure the nano-laminate period (d) dependencies of the Experimentally determined Reaction Front Velocity (m/sec) and the Total Exothermic Energy (kJ/mole atoms) are presented and compared to model calculations for Monel400/Al {$(Ni_{0.7}Cu_{0.3})Al$} nano-laminate structures. The term t_{ab} in the model calculation formulae refers to a reacted zone thickness at the interfaces between the Momel400 and Al formed during synthesis. The formation of this reacted zone decreases the srored chemical energy and has dramatic impact for very small period nano-laminates.

Reaction front velocities from 0.1-100 m/s can be reproducibly and precisely achieved. Nano-laminate reaction temperatures between 200 and >2400 °C are observed for materials with different compositional and structural characteristics. Exothermic heats of reaction from 0.1-1.8 kcal/g are capable with different multilayers.[6-7] There have been several reports of more fundamental modeling of these properties and the influence of structure, composition, and processing conditions. Iin the work reported here the stored chemical energy was expected to be ≈40 kJ/mole atoms and the reaction front velocity ≈ 11 m/s.

We have successfully dip-coated Monel400/Al flash metal multilayer foil with pyrotechnic-based sol-gel materials. Preliminary experiments have indicated that the conversion of a Monel400/Al multilayer to its respective intermetallic generates sufficient energy to ignite the more energetic Fe_2O_3/Al composite booster coating. An idealized scheme of what this material looks like on the microscale is shown in Figure 2.
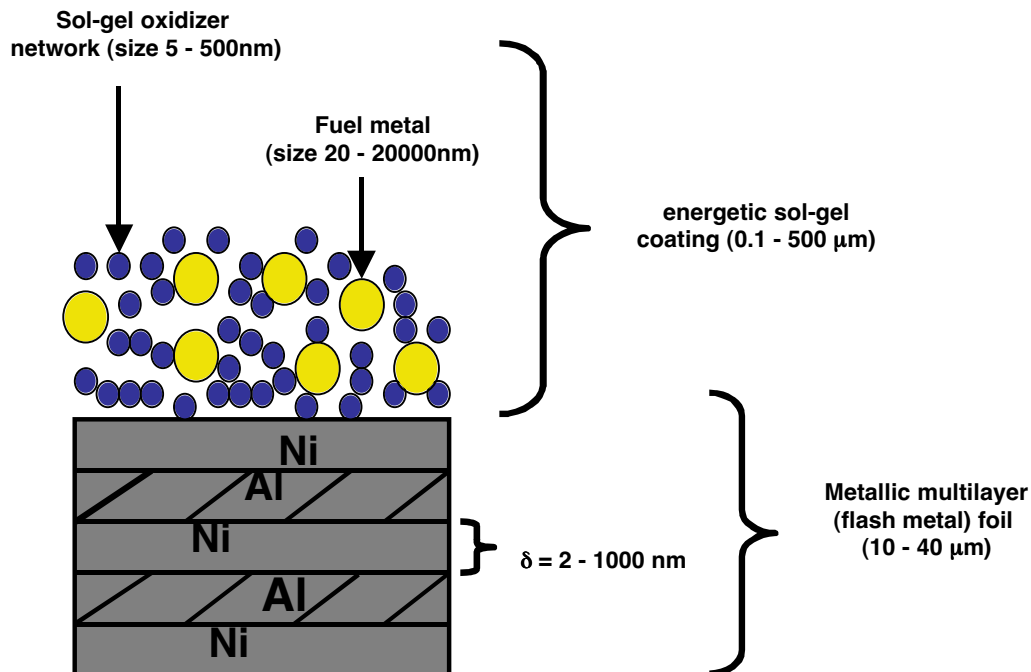
Figure 2. Scheme of microstructure of an energetic sol-gel coated flash metal multilayer nanocomposite for use as new, small, safe, and non-toxic initiators. The proportions of the individual components are not to uniform scale in this schematic figure.

The Fe_2O_3/Al nanocomposites ignite and burn at temperatures exceeding 3000 K. Such composite material(s) have sufficient energy output when ignited to initiate other charges. We have successfully used both ultra fine grained (UFG) nanometer-sized (~30-100 nm diameter) Al and *conventional micron-sized Al* in these types of nanocomposites. It is important to emphasize that these materials can be made successfully using micron-sized Al. Micron-sized Al has been demonstrated to be an effective and reliable component of energetic materials. Although less reactive than the MIC Al, the micron Al has a greater energy density, is safer to work with, and has substantially improved aging properties all of which result in more reproducible performance in applications.

The photo in Figure 3a is that of a Monel400Al multilayer structure foil that has been dip-coated with energetic sol gel material Fe_2O_3/Al. The sol-gel process is also amenable to spin- and spray-coating technologies to coat surfaces.

a)

b)

Sol-gel booster
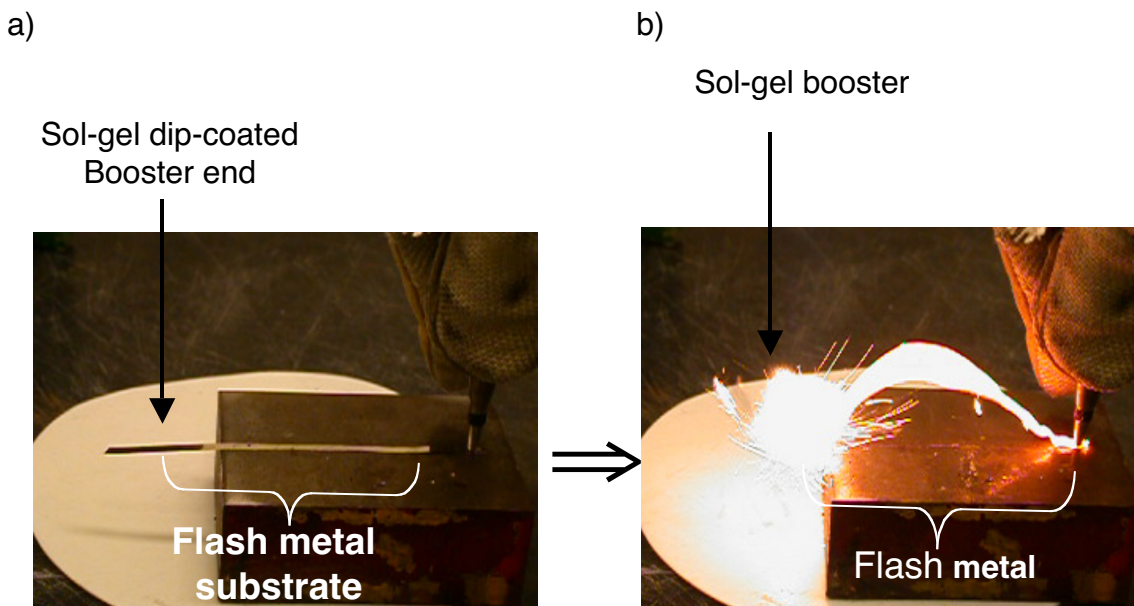
Sol-gel dip-coated
Booster end

Figure 3: a) Sol-gel Fe_2O_3/Al coated Ni/Al multilayer nanocomposite (the coated portion of the multilayer is on the left end of the foil; b) mechanical initiation of the nano/nano composite, using a spring-loaded punch, results in ignition of the energetic sol-gel coating.

In Figure 3b we have used a spring-loaded punch to mechanically initiate the multilayer foil to react. As can be seen from the image, the mechanical stimulus induces the exothermic transformation of the multilayer to its respective intermetallic alloy. The arching glowing foil indicates that the transformation propagates along the foil perpendicular to the punch and migrates to the energetic sol-gel-coated region of the foil. This reaction has sufficient output energy to ignite the more energy dense sol-gel thermite reaction. This particular

thermite reaction is known to reach temperatures in excess of 3100 °C. Other thermite reactions are known to reach temperatures of ~ 4000K.**[16]**

Discussion

The initiation mixture components and their reaction products, from this particular nano/nano composite, are non-toxic, non-hazardous and environmentally benign. The base Fe_2O_3/Al composite and its reaction products Al_2O_3 and Fe metal are frequently used in many common industries on a commodity scale. The precursor compounds utilized in the preparation of the sol-gel materials are prepared from the inorganic metal salts (e.g., ferric chloride and ferric nitrate) are economical, non-toxic, safe, and easy to handle and dispose of.**[14-15]** The solvents used in the synthesis can be water or simple alcohols like ethanol. These solvents are advantageous as they are non-toxic, non-hazardous, cost-effective, and do not pose any major disposal problems. The nano-laminate foil used in this case consists of alternating layers aluminum and Monel400l. The mechanical stimulus initiates the rearrangement of the multilayers to their alloy $Al(Ni_7Cu_3)$ which is an inert safe solid material.

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